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A CATHODE-RAY SPECTROGRAPH FOR STUDYING EMISSION AND ABSORPTION SPECTRA

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1. Introduction

Emission and absorption spectra in the ultra-violet and the visible regions are generally studied by first photographing the spectrum and then measuring the intensities of the lines and bands or the energy distribution in the spectrum by means of a micro-spectrophotometer. In the infra-red region the photographic method can be employed by using specially sensitized plates, only up to about 13,500 A.U. Beyond this wavelength the spectrum can be studied only by means of thermo-electric methods, *viz.*, thermopile, bolometers and radiometers.

These methods generally take a considerable amount of time before the spectroscopic data are available for analysis. An instrument which will give an instantaneous measure of any of the emission or absorption lines and bands in any region of the spectrum will find great application in spectroscopic research especially in industrial spectro-chemical analysis.

The present paper describes such an instrument which presents instantaneously on a cathode-ray tube screen a graph of energy distribution against wavelength corresponding to any spectrum or region of a spectrum which is focussed on the instrument. The instrument can also be used as a spectrophotometer, and any spectrum plate can immediately be examined or measured on the fluorescent screen of a cathode-ray tube.

Recently, descriptions of two instruments by Daly and Sutherland of Cambridge[1] and King, Temple and Thompson of Oxford[2] have appeared. They have developed methods by means of which infra-red absorption spectra can be presented on the fluorescent screens of special cathode-ray tubes which have persistence of the order of 15 seconds. The instrument described here is entirely different in the operating principle and makes use of an ordinary short persistence cathode-ray tube oscillograph. A paper describing the earliest model of this instrument was presented by the present writer at a Symposium on "Atmospheric Processes" held at the Royal

Institute of Science, Bombay, in August 1946.[3] Some later results were summarised in a note published in *Nature*[4] and in communications to the Indian Science Congress in 1946, 1947 and 1948[5, 6, 13].

Here, it is proposed to give a description of the latest model of the instrument which incorporates a number of refinements and new techniques which enable it to be used for quantitative work.

2. Working Principle of the Cathode-Ray Spectrograph

The basic principle of the spectrograph developed by the writer is as follows:—

An ordinary spectroscope is used for forming a sharp image of a spectrum on a slit which is kept in a steady state of oscillation by mechanical means. This scanning mechanism will be described fully in a later section. This slit executes a simple harmonic motion at a frequency which can be varied by adjusting the speed of the driving motor from about 1 to 25 or 30 cycles per second. The light passing through this slit is received by a photoelectric cell which has a cæsiated silver (Cs–CsO–Ag) photocathode. The output of the photocell is fed to a high gain amplifier and then is applied to the vertical deflecting plates of a cathode-ray tube. The vertical displacement of the cathode-ray spot thus becomes dependent on the output of the photo-cell which in turn depends on the intensity of the light passing through the slit to the photocell.

To the horizontal deflecting plates of the cathode-ray tube is applied a voltage which is generated by an electric contact sliding over a potentiometer through which is maintained a steady unidirectional current. As the sliding contact is actuated by the movement of the scanning slit itself, the voltage of the sliding contact undergoes a variation which follows the movement of the slit and has the same frequency as the oscillation of the slit. The output of this potentiometer is amplified by a direct coupled amplifier and then applied to the horizontal deflecting plates of the cathode-ray tube. Thus, the horizontal displacement of the cathode-ray spot is controlled by the movement of the slit.

Now, when the instrument is in operation, the slit oscillates in the spectrum at a certain frequency. As the horizontal displacement of the spot is controlled by this movement of the slit, the spot on the screen oscillates horizontally in synchronism with the slit. At the same time, the spot is undergoing also a vertical displacement which is dependent on the intensity of the light passing through the slit at any given instant. As the slit moves along the spectrum, the intensity of the light undergoes a change according

to the energy distribution in the spectrum being scanned. The cathode-ray spot thus gets a vertical deflection which corresponds to this energy distribution in the spectrum. The presence of any emission or absorption lines or bands in the spectrum produces an increase or decrease in the photoelectric current which is followed faithfully by the cathode-ray spot. The spot thus traces a curve on the screen of the cathode-ray tube, which is a graph of light intensity against wavelength in the region of the spectrum being scanned, the emission or absorption lines appearing as humps or dips respectively on this curve. The height or depths of these humps and dips obviously depend on the intensities of the emission or absorption lines. Fig. 1 gives a schematic circuit diagram of the complete cathode-ray spectro-

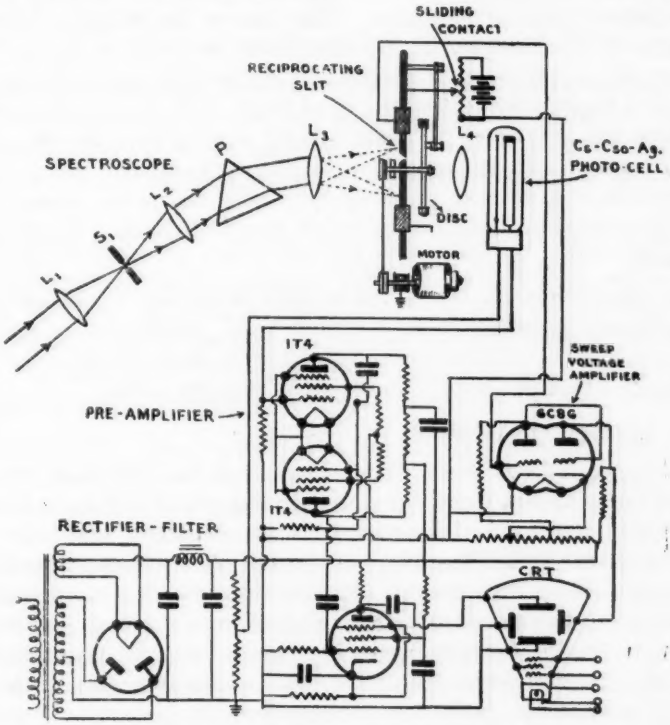

FIG. 1. Schematic Circuit Diagram of Cathode-Ray Spectrograph

graph as this apparatus is named. Figs. 7, 8, 9,10, 12 and 13 show the type of patterns produced on the fluorescent screen by means of the cathode-ray spectrograph.

3. Description of the Cathode-Ray Spectrograph

The complete apparatus is made up of the following five units:—

(i) The spectroscope,
(ii) The scanning mechanism,
(iii) The photocell and amplifier,
(iv) The synchronising voltage generator and
(v) The cathode-ray oscillograph.

Each group will be described here in outline.

(i) *The Spectroscope*

The spectroscope used in this apparatus is of the ordinary type with an equilateral prism of flint glass. The base of the prism is 7·8 cm. and its height 4 cm. Sunlight or the light from an artificial source like the mercury arc, pointolite or a sodium arc is focussed on a bilateral slit by means of a 3-inch glass lens with a focal length of 8 inches. An achromatic compound lens collimates the beam of light coming from the slit. Another achromatic lens with an adjustable diaphragm focusses a sharp image of the spectrum at a distance of about 18″. With the prism adjusted for the angle of minimum deviation the visible spectrum covers a length of about 2·5 inches.

The glass prism and the system of glass lenses used in this spectroscope have sufficient transmission up to about 1·5 μ, which can be utilised for studying a number of absorption bands due to atmospheric water vapour and oxygen which are present in the near infra-red region.

(ii) *The scanning mechanism*

During the various stages of development of the instrument the author has used in succession three types of scanning device for the cathode-ray spectrograph, *viz.*, (*a*) a slit mounted on an oscillating steel reed excited by an electromagnet at 50 cycles per second, (*b*) a rotating scanning disc with a single slit or a number of identical slits and (*c*) a reciprocating slit driven by an adjustable speed motor. Out of these the first two have been discarded in favour of the reciprocating type in the final instrument. But for the sake of completeness and as it helps in giving some idea of the design problems encountered during the development of this spectrograph, they will be described here briefly.

(*a*) *The Oscillating reed.*—In this scanning mechanism the slit is mounted on a thin steel reed which is fixed at one end. The length of the reed is such that it has a natural frequency of oscillation of 50 cycles per second. The

reed is maintained in a steady state of oscillation by an electromagnet excited from the 50 c.p.s. mains supply. The arrangement gives an amplitude of oscillation of about 1·5 cm. Fig. 2 shows the sketch of the arrangement.

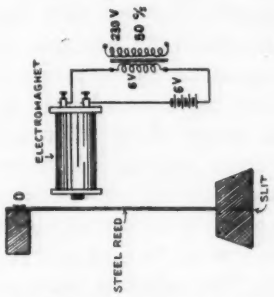

FIG. 2. Sketch of Oscillating Reed Type Scanning Mechanism

The battery provides a d.c. bias on the 50 cycles per second exciting voltage so that the pull exerted on the reed operates only during half a cycle. If a pure alternating current is used the reed gets an excitation of 100 c/s as the electromagnet pulls during both the positive and negative halves of the cycles.

When the oscillating reed is used the voltage for the horizontal sweep of the cathode-ray spot is also obtained from the 50 cycles per second mains. But, for an exact synchronism between the motion of the scanning slit and the horizontal sweep of the cathode-ray spot which is essential for the satisfactory reproduction of the graph on the screen of the cathode-ray tube, it is necessary that the sweep voltage is in phase with the motion of the slit.

Although this scanning was found to be fairly satisfactory for examining narrow regions of the spectrum at a time, it had several defects. The slit was truly vertical only when it was in its normal position during the course of the oscillation. When it was pulled out by the electromagnet it was not parallel to the lines in the spectrum, but made a slight angle. This was equivalent to an effective increase in the scanning slit width and resulted in loss of resolution towards the edges. Thus, the true intensities of the lines could only be estimated in the centre of the pattern produced on the cathode-ray tube; and any band which had to be measured must first be centred on the screen. The second defect was that a base line corresponding to zero intensity of light could be produced if only one half of the oscillation of the slit was used for scanning and during the other half light was not allowed to pass through the slit. This not only reduced the already small scanning range of the slit but also necessitated the shifting of phase of the sweep

voltage through a large angle in order to get the base line on the screen in the correct position. This resulted in a certain amount of distortion in the horizontal plane, *i.e.*, the wavelength scale was distorted.

Another difficulty experienced was that due to the high speed of scanning the output of the photo-cell contains very high frequency components, especially if the region of the spectrum being scanned contains a number of sharp absorption bands and lines. In order to deal with such high frequencies the input circuit of the photo-cell amplifier requires great care in designing and a certain amount of compromise has to be made in choosing the load resistance for the photo-cell in relation to input capacitance of the first valve and its grid current. A high load resistor which is desirable for high sensitivity cannot be used as it results in a low amplification at the higher frequencies. This effect is very pronounced if an ordinary radio amplifier is used as the input valve. It can, however, be greatly reduced by using special tubes of the miniature and electrometer type which have extremely low input capacitances and low grid currents. As none of these special tubes are available in India at present, we had to be satisfied by reducing the load of the valve and making up for this loss of gain by extra amplification in later stages. This, however, is not the best arrangement, as it greatly increases the noise of the amplifier which appears as a wavy pattern superimposed on the graph.

Except for these defects the arrangement was satisfactory and gave steady patterns on the cathode-ray screen which could be examined with great ease, especially while working with the bright solar spectrum.

(*b*) *Rotating Scanning Disc.*—This consists of a metal disc with a diameter of about 12 inches and with a number of identical slits cut near the edge of the disc which are about an inch apart. Fig. 3 gives a sketch of the scanning disc. The disc is mounted in such a way that the spectrum is focussed on these slits. As the disc is rotated by means of a small electric motor, the spectrum is scanned by the slits which move across the spectrum in succession. By placing a rectangular window whose length is exactly equal to the distance between the slits, the spectrum is scanned by only one slit at a time. As one slit moves out of the window, the next one appears at the other edge. This arrangement had certain advantages over the oscillating reed type of scanning. Firstly, by making the diameter sufficiently large the error due to the change of angle of the slit due to rotation can be greatly reduced, which gives better resolution at the edges. In a large disc of about 15″ diameter, it is possible to keep the distance between the slits as large as 1·5 inches without introducing serious error due to change of

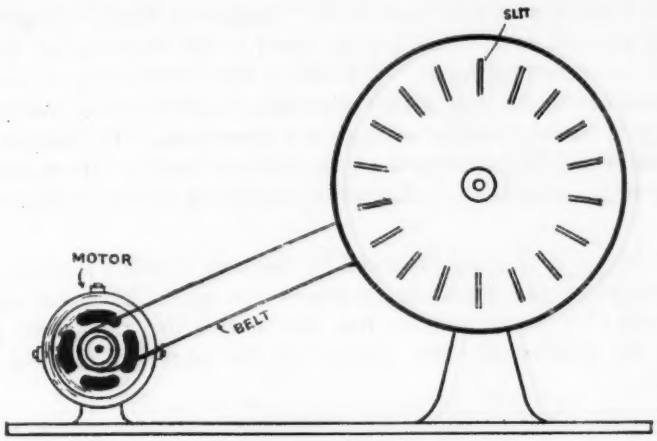

FIG. 3. Rotating Disc Type Scanner

slit angle at the edges. Thus a larger portion of the spectrum can be examined at a time.

The main difference between the rotating disc and the oscillating reed type of scanning, however, is in the type of motion of the slits. While in the oscillating reed type the slit executes a simple harmonic motion, the slits in the rotating disc have a uniform and almost linear motion. The voltage with a sinusoidal waveform used for producing the horizontal sweep in the reed type of scanning is quite unsuitable for this rotating disc type of scanning. The linear motion of the slit in this type of scanning requires a sweep of a wave form of the type known as the " saw tooth " type (Fig. 4)

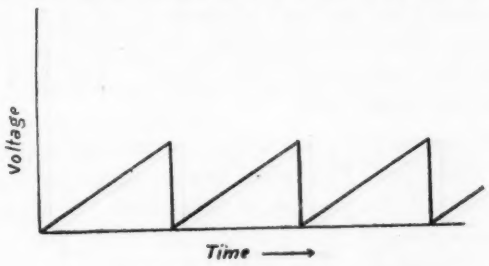

FIG. 4. ' Saw Tooth ' Wave Form

which is generally used for the time base in cathode-ray oscillography. Most modern cathode-ray oscillographs are provided with a " saw tooth " oscillator of this type which can be used for this purpose.

The frequency of this "saw-tooth" horizontal sweep voltage must be carefully adjusted so as to be exactly equal to the frequency at which the spectrum is scanned by the slit. The motor used for rotating the disc should be of the synchronous type so that once the adjustment of the sweep voltage frequency is made it should remain in synchronism. In addition to this the output of the photo-cell itself can be used for 'locking' the sweep voltage with the signal, thus holding the pattern stationary on the cathode-ray tube screen.

The base line is easily produced by masking alternate slits on the disc, but keeping the sweep voltage frequency the same. The spot traces the curve during one cycle and the base line during the next, when no light reaches the photo-cell. No shifting of the phase is required in this system.

One great difficulty which was experienced with this system is that to get a perfectly steady graph on the screen it is absolutely essential that all the scanning slits on the disc must be optically identical, and the distances separating them must also be exactly equal. This, however, may not prove to be a problem of great difficulty if such slits are produced by some type of photo-engraving method or are cut with an accurate punching machine. If the slits are not identical each slit traces a curve which has a different amplitude, and on the screen is seen a multitude of graphs instead of a single steady pattern. If photographic record only is required and no visual examination is to be made this difficulty can be overcome by using a single slit on the disc.

(*c*) *The Reciprocating Slit Scanner.*—All the problems and difficulties encountered in the oscillating reed and rotating disc type of scanning are solved in the reciprocating slit type of scanning which in conjunction with its automatic sweep voltage synchronising arrangement produces a perfectly steady pattern on the cathode-ray tube screen. Fig. 5 shows a sketch of this type of scanning mechanism.

D is a metal disc which is coupled to a small electrical motor by means of a pulley and string belt. The motor has an adjustable gear ratio mechanism so that the speed of the disc can be varied from 1 to about 30 revolutions per second. P is a smooth and well-polished metal plate which can slide freely in the metal frame F. This plate P is coupled to the rotating disc D by means of a coupling shaft C which has loose joints at A and B. The coupling arrangement is similar to that used in the ordinary reciprocating engine. The rotatory motion of the disc is communicated to the plate which slides back and forth in the frame F, and executes a simple harmonic motion.

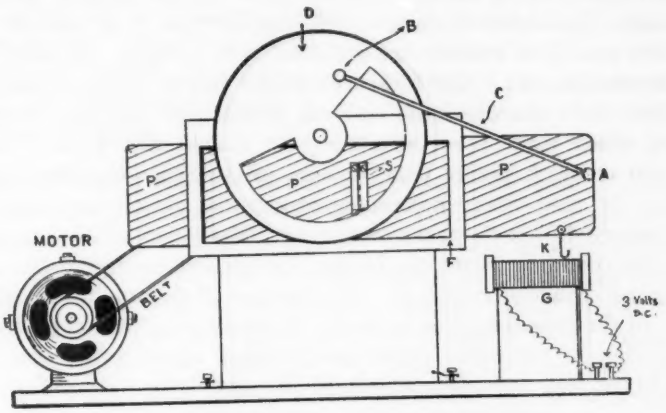

FIG. 5. Reciprocating Slit (Scanning Mechanism)

On this plate is mounted an adjustable slit S which oscillates when the motor is switched on. The spectrum is focussed on this slit.

It will be noticed from Fig. 3 that a circular slot has been cut in the disc D. This arrangement makes it possible to obtain the base line corresponding to the zero light intensity for the graph traced on the cathode-ray screen. This slit allows the light passing through the slit to reach the photocell only when the slit is passing from left to right, while on its return journey the light is cut out by the opaque portion of the disc.

Attached to the plate P is a sliding electrical contact K which moves over the potentiometer G and generates the horizontal sweep voltage. The function of this mechanism will be explained later on. All that this mechanism does is that it keeps the slit oscillating at any desired frequency, cuts out the light passing through the slit during half the cycle of oscillation and generates a sweep voltage which has the same waveform, phase and frequency as the motion of the slit.

The error due to change of angle is absent in this scanning mechanism as the slit remains vertical throughout the cycle. The sweep voltage is produced by the movement of the slit itself so that the two are automatically in perfect synchronism. Any drift in the speed of the motor, therefore, does not upset the synchronization.

(iii) *The Photoelectric cell and Pre-amplifier*

The light passing through the scanning slit is received by the photoelectric cell. Any photoelectric cell of the vacuum type, sensitive in the

spectral region to be studied may be used. In the present instrument 3 photo-cells have been tried, *viz.*, 918, GL 929 and 71 A visitron. Out of these 918 and 71 A visitron are gas filled type of cells. GL 929, however, is of the vacuum type. Gas filled cells have a greater sensitivity than vacuum cells, but their characteristics are not stable and undergo unpredictable changes which make them unsuitable for quantitative work. Their noise level also is much higher than vacuum photo-cells. Gas-filled cells may, however, be used where percentage absorption in any particular band is to be measured as such measurements are independent of the characteristics of the photosensitive element. In fact, the present apparatus was originally developed in connection with our investigation of the total precipitable water vapour of the atmosphere as estimated by measuring the percentage absorption in some of the water vapour bands which occur in the near infra-red region of the solar spectrum between 0·75 μ and 1·3 μ. (See Figs. 7 and 8.)

The output of the photoelectric cell has to be amplified several thousand times before it will have sufficient strength to produce the required deflection of the cathode-ray spot. This amplification is achieved by means of a high gain amplifier. The amplifier consists of two main sections, *viz.*, (i) the pre-amplifier which forms a part of the photo-cell pick-up assembly and (ii) the main amplifier which may form a part of the cathode-ray tube assembly.

(i) *The Pre-amplifier.*—The design of the pre-amplifier presents some special requirements which have to be met in order to obtain the desired amount of detail in the record produced on the cathode-ray tube screen. When a spectrum containing a large number of lines and bands with various intensities is scanned the output of the photoelectric cell may contain frequencies which may be as high as 50 kilo-cycles per second. Therefore, the amplifier must be designed to have a gain which is constant from about 50 kc/s down to the frequency of the scanning slit oscillation (*i.e.*, the repetition frequency of the trace) which may be sometimes as low as 2 or 3 cycles per second. The main difficulty in this respect arises if the load resistor of the photo-cell is very high and the input capacity and grid current of the first valve of the pre-amplifier are also high. At the same time as high a load resistor as possible is desirable, for, the sensitivity of the photo-cell circuit increases with the value of the load resistor up to a certain limit. But unfortunately an increase in the load resistor decreases the response of the amplifier at higher frequencies, especially if the input capacity of the first valve is also high. An increase in the load resistor increases the time constant of the input circuit and thus its response to frequencies which have a shorter period than this time constant is poorer. With a load resistor of

about 40 Megohms and a 6 J7G as the input tube it was found that a certain amount of detail in the record did not appear on the cathode-ray tube screen. But if the speed of scanning is reduced, which is equivalent to reducing the effective frequencies corresponding to this finer structure of the curve, the detail again appears in the graph, as it now comes within the range of the amplifier.

The load resistor had therefore to be reduced to about 4 to 6 Megohms for a satisfactory performance, although this resulted in a considerable loss in the sensitivity. An attempt to make up for this loss by adding additional stages of amplification was not very successful as each additional stage adds to the general noise level of the amplifier, and the ' mush ' appears superimposed if the spectrum to be spectrum to be studied is weak, requiring the use of the full gain of the amplifier. By using a miniature tube (IT4) as the input valve the load resistor could be increased to a value of about 15 Megohms without appreciable loss in the detail of the graph, *i.e.*, loss of response at the higher frequencies.

The pre-amplifier which uses IT4 type tubes was mounted on a small aluminium chasis together with the photoelectric cell, and the whole assembly was enclosed in a small aluminium box with a rectangular slot equal in size to the photo-cell cathode cut into its side so that the light passing from the scanning slit could reach the photocathode. It was necessary to enclose the whole pre-amplifier assembly in a metallic box as it is very important to shield the photo-cell circuit from all stray fields and electrical pick-up, which are present in all electrified areas. If this stray pick-up is not carefully excluded from the input circuit of the amplifier by shielding as described above, it appears after amplification with the desired signal and with almost comparable amplitude, making it difficult to distinguish the signal from the pick-up. The connections to the high tension and low tension voltage supplies are made through shielded flexible wires. The output of the amplifier is also transmitted to the main amplifier through a shielded cable. The metal box and the shields of the connecting cables are earthed properly.

Another precaution which has to be taken is to keep the value of the coupling condenser between the two IT4 stages of the pre-amplifier consistent with the frequency response desired. Too low a value of the coupling condenser produces a peculiar effect which is illustrated in Figs. 6 (*a*) and 6 (*b*). If a voltage pulse with a wave form as in 6 (*a*) is applied to the input of amplifier, the output waveform takes the shape shown in 6 (*b*). With a value of 0·2 μfd this effect was reduced to a negligible value. The explanation of this effect is again to be found in the time constant of the

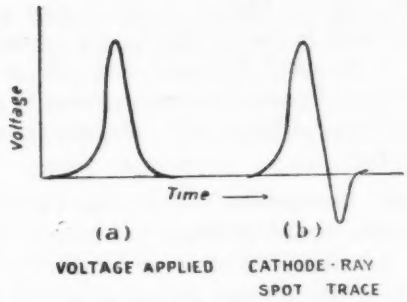

FIG. 6. Effect of Low Coupling Capacity

circuit formed of the load resistors, coupling capacity and the grid resistor in the circuit.

(ii) *The main amplifier.*—This is of conventional design and should have a frequency range sufficient to cope with the signal delivered by the pre-amplifier. The built-in amplifier of a DuMont Cathode-Ray Oscillograph Model 208, was found to be quite satisfactory.

(iv) *The horizontal sweep voltage generator*

In the reed type of scanning slit and in the rotating disc the horizontal sweep voltage was usually obtained from a source which was independent of the motion of the scanning slit. It was necessary, therefore, to provide means for accurately synchronising the motion of the slit with the sweep voltage. It was also necessary to see that the wave form and phase of the sweep voltage exactly corresponded with the motion of the slit.

In the reed type of scanning it was generally found necessary to shift the phase of the sweep voltage in order to obtain synchronisation. This was achieved by passing the sinusoidal sweep voltage through an adjustable phase shifting network. The frequency of the mains supply was also found to undergo small irregular variations which added to the difficulties of obtaining a perfect synchronisation.

In the rotating disc type of scanner where the linear sweep voltage was obtained from a 'saw-tooth' oscillator, the slightest variation in the speed of the motor would upset the synchronisation and an adjustment of the oscillator frequency had to be made, until synchronism was established again. It was therefore felt that some arrangement should be provided by means of which the motion of the slit itself produced the sweep voltage, so that the wave form and the frequency of the sweep voltage will be identical

with the motion of the slit and an automatic synchronisation will be obtained. This has been achieved by means of the arrangement described below.

As will be seen in Fig. 5 on the projecting end of the plate P which oscillates in the frame F is mounted a spring contact K which slides over a wire-wound power resistor. A steady unidirectional current is made to flow through this resistor by connecting a battery of about 3 volts to 6 volts as shown in the diagram. One end of the resistor is earthed. Now, as the sliding contact moves over the resistor winding it undergoes a variation in potential. As the movement of the slider is produced by the movement of the slit itself, the waveform, frequency and phase of this variation of potential are exactly identical with those of the slit motion. Any change in the frequency of the slit is faithfully followed by the slider potential. This potential is applied to the input valve of a direct coupled amplifier and then applied to the horizontal deflecting plates of the cathode-ray tube. A slight ripple developed by the slider jumping over the windings of the resistor is easily filtered out by means of a condenser connected across the load resistor of the valve. A value of about ·25 μfd was found to be quite satisfactory for this purpose.

(v) *The Cathode-Ray Oscillograph*

The pre-amplifier delivers a sufficiently high output with spectra of normal brightness to be used for the direct application to the deflecting plates of a cathode-ray tube, and it does not become necessary to use any additional amplification except in cases where weak spectra produced by laboratory sources are being studied. It is therefore not absolutely essential to use a complete Cathode-Ray Oscillograph with its built in amplifiers and auxiliary equipment. But if an Oscillograph is available, it is advantageous to use it in view of the great ease of adjustment that is possible with the various controls that are provided in a modern oscillograph, and the built in amplifiers provide a reserve of amplification which is very useful for studying weaker spectra.

A DuMont 208 model Cathode-Ray Oscillograph was used in the present investigation and was found to give very satisfactory results. This Oscillograph has a five-inch screen. The Y-axis amplifier has a gain of about 2,000 with almost linear frequency response up to about 30 kc/s. The X-axis amplifier has a gain of about 50 which is quite sufficient as a sweep voltage input of up to 10 volts can easily be obtained by connecting a suitable battery across the potentiometer, in the scanning mechanism. A special circuit used in the oscilograph for the rapid vertical and horizontal positioning of the pattern is very useful. A transparent graph scale which

can be attached to the screen makes it possible to make direct measurement of absorption on the screen.

4. Performance of the Cathode-Ray Oscillograph

Figs. 7, 8, 9, 10, 12 and 13 give the patterns produced on the screen when various spectra were being scanned.

Fig. 7 shows the near infra-red spectrum of sunlight. The absorption bands due to atmospheric water vapour and oxygen can be seen clearly. The bands from left to right are due to water vapour ($\cdot 73\,\mu$), oxygen ($\cdot 76\,\mu$), water vapour ($\cdot 79\,\mu$), water vapour ($\cdot 93\,\mu$) The percentage absorption in any of these bands can be measured immediately on the cathode-ray tube screen. It may be mentioned that the cathode-ray spectrograph was primarily developed for such measurements in the ρ and ϕ bands at $\cdot 93\,\mu$ and $1 \cdot 13\,\mu$ respectively for the estimation of the total water vapour content of the atmosphere. The increase in air mass traversed by the solar rays in the morning or evening produces an appreciable deepening of these absorption bands. The changing amout of water vapour in the atmosphere from day to day is very strikingly reflected in the changes in the depths of these bands. A comparison of Figs. 7 and 8 will bring out this effect clearly. Fig. 8 was photographed on a clear afternoon in January 1947 while Fig. 7 was taken just before the onset of the monsoon in June 1947. The deepening of the band is quite pronounced, while the oxygen band is unaffected.

Fig. 9 shows the oxygen band at $\cdot 76\,\mu$ which has deepened towards evening due to the increase in air mass traversed by sunlight.

Fig. 10 shows the emission spectrum of a low intensity mercury arc. The lines shown in the diagram are from left to right, yellow $\cdot 5780\,\mu$, green $\cdot 5461\,\mu$, blue $\cdot 4916\,\mu$ and violet $\cdot 4358\,\mu$.

The intensities appearing in the graph are not the true intensities of the lines but those modified by the spectral response of the photo-cell and the transmission of the optics of the spectroscope. It is however possible to prepare a simple table of correction to be applied at various wavelengths by making use of the spectral response curve of the photoelectric cell used with the spectrograph. Another simple method of eliminating the error due to photo-cell characteristic is to use a mask of the same shape as the spectral response curve of the photo-cell in front of the photo-cell window. For example, Fig. 11 gives the response curve of a typical photocell with a cæsium cathode. Now if a window having the shape of the shaded area in the above curve is cut into a mask and is placed before the photo-cell, it

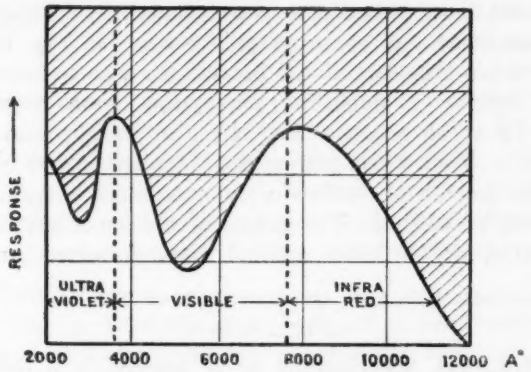

FIG. 11. Spectral Response of Cs–Cso–Ag Photocell

(Shaded area shows the shape of the window used for correcting the spectral response of the cell)

will be seen that more light will be allowed to reach the photo-cells at wavelength, where it has a poorer response and the amount of light passing to the photo-cell at wavelengths where it has better response will be reduced. Thus the output of the photocell can be made almost linear in the whole of the spectrum.

With such a mask used, the amplitudes of the various lines appearing on the fluorescent screen will correspond to their true intensities.

Fig. 12 shows the absorption at ·66 to ·68 μ due to chlorophyll dissolved in acetone. The characteristic absorption band can easily be recognised by those who are familiar with chlorophyll spectra. As sunlight has been used in this measurement, the chlorophyll band appears superimposed on the solar spectrum. The atmospheric oxygen band at ·76 μ can also be seen clearly beside the chlorophyll band.

These experiments demonstrate the utility of the Cathode-Ray Spectrograph for the rapid measurement of absorption in solutions and pigments of this type. Similarly, the transmission characteristic curves of any optical filter can immediately be recorded on this instrument.

Fig. 13 (*a*) shows the pattern produced when the image of a spectroscopic negative (from an original by R. S. Krishnan) showing the second order Raman spectra in diamond is projected on the scanning mechanism of the Cathode-Ray Spectrograph. The pattern produced may be compared with the microphotometer record of the same negative made with the conventional microspectrophotometer (Fig. 13 *b*). The Cathode-Ray

Spectrograph can thus be used as a spectrophotometer for the rapid examination or measurement of spectrographic plates. In Fig. 13 (*a*) the exact intensities have not been reproduced because the negative used was obtained by re-photographing a published photograph from a paper by R. S. Krishnan.[7] Thus the negative used does not exactly correspond to the original negative from which the microphotometer record (Fig. 13 *b*) has been made, on account of the loss of contrast which usually takes place in the photo-block processing. The shapes of the bands and lines, however, compare satisfactorily with the original microphotometric record.

5. Possible Further Development of the Cathode-Ray Spectrograph

The Cathode-Ray Spectrograph in its present form can be used for exploring the spectral region between about $\cdot 34\,\mu$ in the near ultra-violet and about $1\cdot 7\,\mu$ in the near infra-red. It is thus possible to make measurements of the emission and absorption spectra with sunlight and laboratory sources like the sodium and mercury arcs, pointolites, etc. The spectral absorption of glass filters, dyes and some organic solution like chlorophyll from plants, etc., can also be studied with this instrument. The Cathode-Ray Spectrograph can also be used for the rapid examination and measurement of spectroscopic negatives.

The main limitations of the present model of the Cathode-Ray Spectrograph are its rather restricted spectral range and its low dispersion. In the ultra-violet the limit is set by the glass optics of the spectroscope used which transmit littl below about $0\cdot 34\,\mu$. In the infra-red the photoelectric cell is the limiting factor. Most commercially available photo-cells with Cs–CsO–Ag cathodes have their long wave thresholds at about $1\cdot 2$ to $1\cdot 5\,\mu$. Some special tubes with quartz envelopes can be used up to about $1\cdot 7\,\mu$.

Recent developments in the making of photoconductive cells have, however, extended the longwave threshold up to about $6\,\mu$,[8, 9, 10, 11, 12] thus bringing this infra-red region also within the reach of photo-cells. It is hoped that it will soon be possible to make these new types of photo-cells which make use of extremely thin semi-conducting layers of lead selenide and telluride. By using these cells the region between 1 to $6\,\mu$ which contains the vibration-rotation bands of the hydro-carbon group and the hydrogen halides will come within the range of the Cathode-Ray Spectrograph. This will make the instrument a very powerful laboratory tool in the hands of the chemist and the industrial physicist who has to deal with chemical process controls in the laboratory, factory or refineries. The special application of this instrument in the petroleum industry is obvious.

As regards the dispersion of the spectroscope used in the present model it is adequate for the near infra-red region where it is being used for the estimation of the water vapour content of the atmosphere by measuring the percentage absorption in the ρ band ($0{\cdot}93\,\mu$) and ϕ band ($1{\cdot}13\,\mu$). A further increase in the dispersion of the spectroscope requires a corresponding increase in the sensitivity of the photo-sensitive element. The ultimate limit of the sensitivity of the photo-cell is, however, set by the noise level in the photo-cell circuit due to thermal agitations and 'shot' effect, etc. This limit has almost been reached in the amplifier where the highest usable gain has been obtained.

A further increase in dispersion in the visible and ultra-violet region is, however, possible if photomultiplier type of cells are used. In these cells the primary emission from a photocathode is multiplied as much as a hundred thousand times by secondary emission from a series of anodes maintained at increasingly high positive potentials. The inherent gain of such tubes using about 9 secondary emission stages can be as high as 150,000 with a comparatively much smaller increase in the noise level. Thus the limitation imposed by the noise level in the ordinary photo-cells will be removed and it will be possible to study extremely weak spectra at high dispersion. In fact, cells of this type have been used for detecting Raman lines[14, 15] which by ordinary methods require hours of exposure with sensitive plates. Work along these lines is in progress.

Acknowledgements

In conclusion, I wish to express my sincere thanks to Dr. L. A. Ramdas, Director of Agricultural Meteorology, for the facilities, encouragement and guidance given to me during the course of this investigation. My thanks are also due to Mr. S. P. Venkiteshwaran, Meteorologist-in-charge of the Instrument Section, for the loan of the DuMont Oscillograph, photographic equipment and facilities in the Meteorological Office Workshop.

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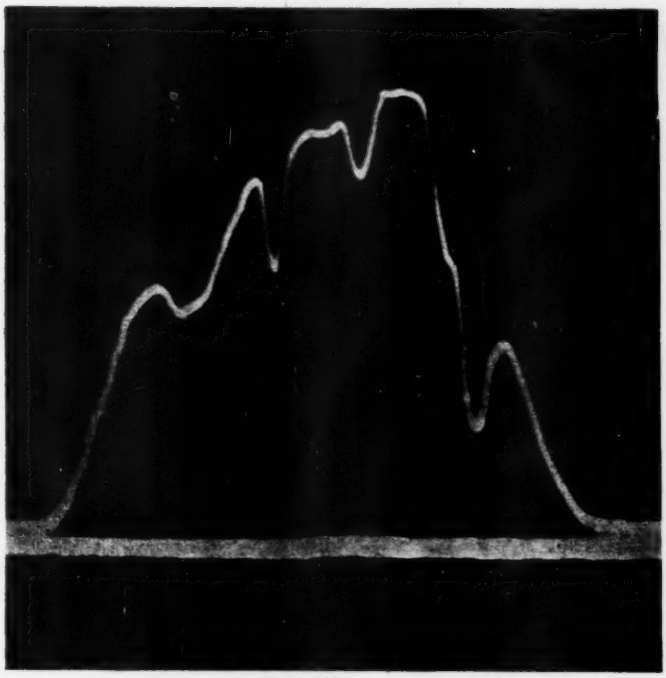

FIG. 7. Absorption bands due to atmospheric oxygen and water vapour in the near infra-red solar spectrum. (June 1947)

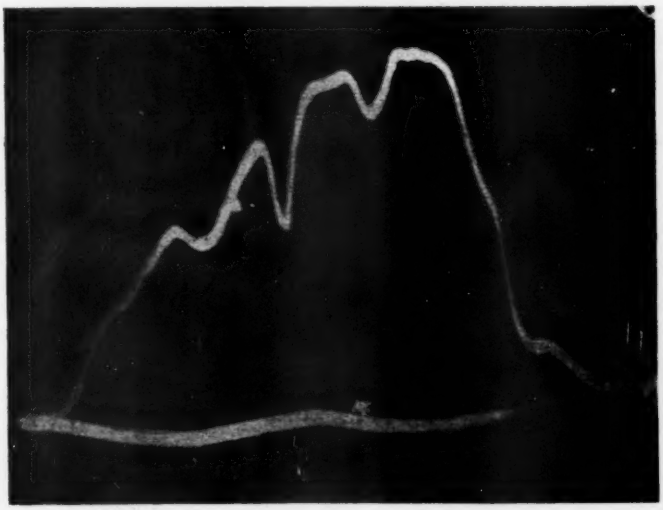

FIG. 8. Absorption bands due to atmospheric oxygen and water vapour in the near infra-red solar spectrum. (January 1947)

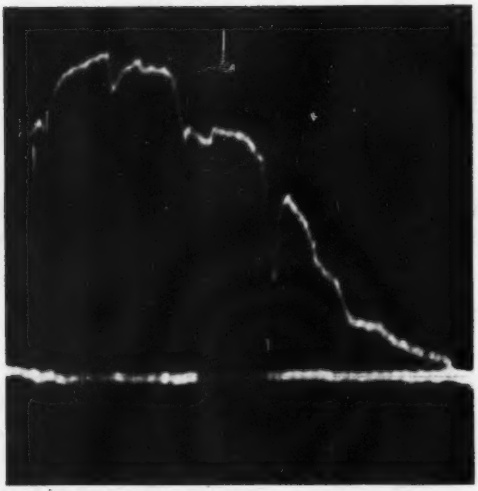

FIG. 9. Absorption due to atmospheric oxygen at 0·76 μ in the solar spectrum.

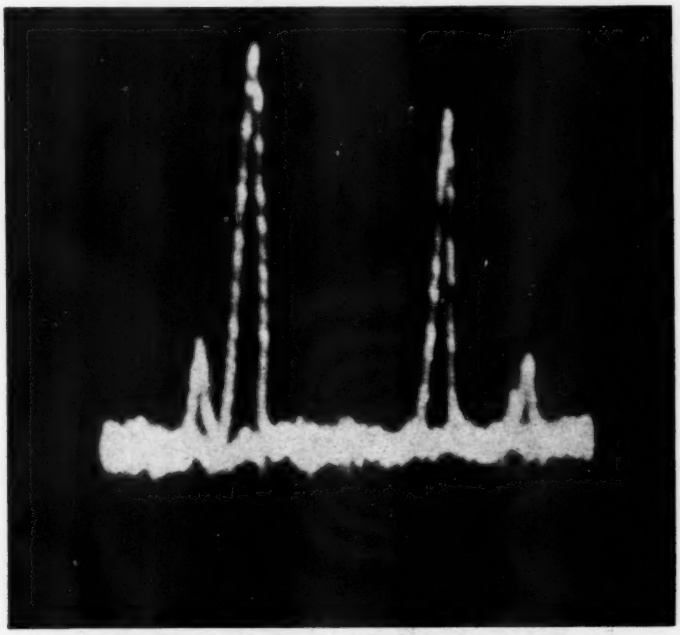

FIG. 10. Emission lines of a low intensity mercury arc.
(From left to right : 0·5780 μ, 0·5461 μ, 0·4916 μ, and 0·4358 μ.)

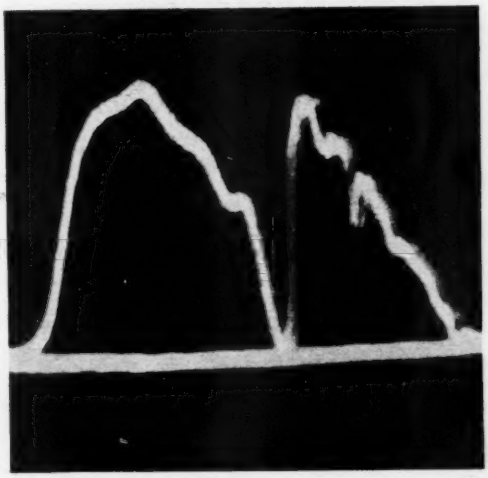

FIG. 12. Absorption in chlorophyll at 0·66 to 0·68 μ.

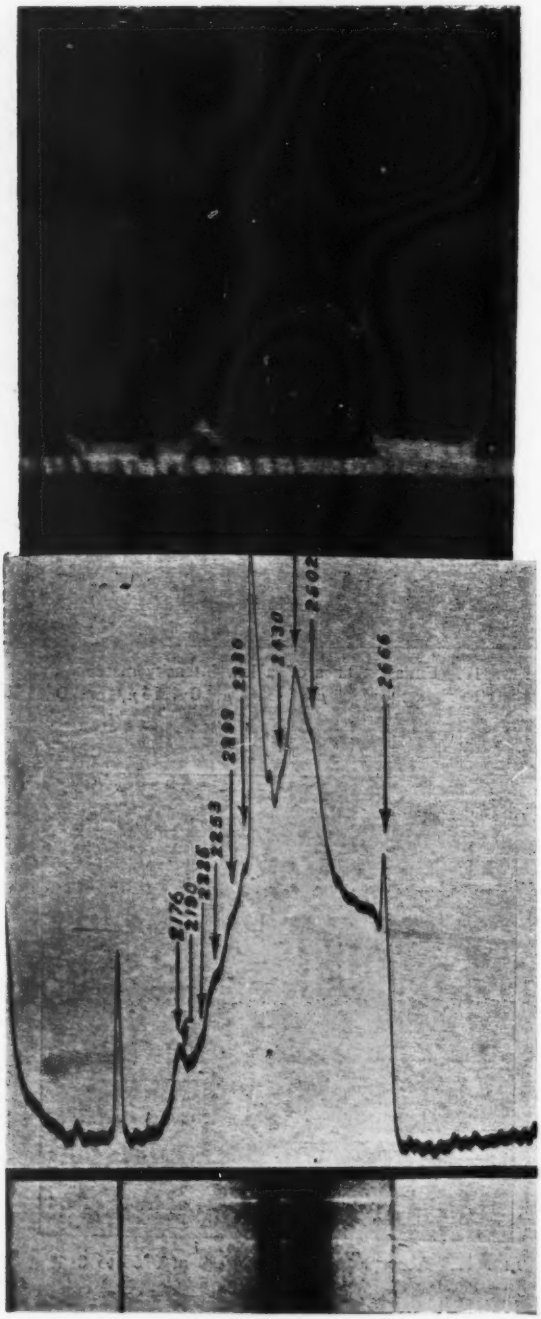

FIG. 13. Use of the Cathode-Ray Spectrograph as a Micro-Photometer.

CHEMICAL EXAMINATION OF JACK TREE LATEX AND JACK FRUIT GUM

Part III. Ultra-Violet Absorption Spectra of Artostenone and α-Artostenone

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Received April 29, 1948

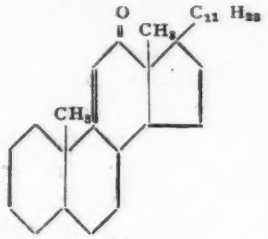
As the result of the earlier work of Nath[1] and of the more recent study of Balakrishna and Seshadri[2] it has been established that artostenone and α-artostenone are isomers which are capable of interconversion.

$$\text{artostenone} \underset{\text{alkali}}{\overset{\text{acid}}{\rightleftharpoons}} \alpha\text{-artostenone}$$

The most characteristic difference between the two lies in the fact that the former does not give rise to enol-esters whereas the latter undergoes this change. Another difference which has been pointed out earlier by Nath is with regard to the capacity to condense with benzaldehyde. α-Artostenone gives the benzylidine derivative and therefore has a reactive methylene group whereas artostenone itself does not undergo this condensation and is therefore devoid of the reactive methylene group. Thus the capacities to form enol-esters and to condense with benzaldehyde go together. With a view to understand the relationship more closely, the ultra-violet absorption spectra of these two substances and of α-artostenone-enol-benzoate have now been studied. Because of the low solubility of the substances in alcohol, ether was used as solvent; the time of exposure was three minutes. The results are recorded below:

Substance	Concentration %	Absorption
Artostenone ..	1·5	235–250 mμ
	2·0	235–250 mμ
	2·5	235–250 mμ and 275-310 mμ
α-Artostenone ..	1·5	235–250 mμ and 288–290 mμ
	2·0	235–250 mμ and 285–292 mμ
	2·5	235–250 mμ and 281–300 mμ
α-Artostenone-enol benzoate	1·5 2·0 2·5	Complete absorption upto 300 mμ

It is remarkable that the spectra of the two isomeric ketones resemble closely. Both possess the high intensity absorption in the region of 240 $m\mu$ which is considered to be characteristic of the $-C=C-C=O$ group. There is some difference in regard to the low intensity band round about 290 $m\mu$. In artostenone this could not be observed with solutions of lower concentrations and at higher concentrations the band is somewhat broader whereas with α-artostenone this could be seen in all the concentrations employed. Thus both the isomers seem to belong to the category of α-β-unsaturated carbonyl compounds. Nath has already reported other experimental results suggesting the presence of this structure in artostenone. It is now clear that even α-artostenone has this grouping. This point is of considerable importance in the consideration of the structure of these compounds. The formula (I) already proposed by Nath for artostenone does not appear to be capable of explaining this isomeric change.



(I)

The enol-benzoate of α-artostenone differs markedly from the two ketones in its spectrum. Its total and somewhat strong absorption up to 300 $m\mu$ should be attributed to the presence of a benzoyl group and two ethylenic bonds.

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THE DEPOLARISATION OF LIGHT SCATTERED BY SOLS

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1. Introduction

Of the various optical properties of colloids one of the most important and the most widely studied is the Tyndall Effect. According to Rayliegh's theory of light scattering, it is to be expected that light scattered in a direction normal to the incident beam is completely polarised. On account of the various assumptions made in the theory, the law cannot be expected to hold in the case of colloids. In fact, it is found that the light scattered in a direction normal to the incident beam is not completely polarised. The degree of depolarisation of scattered light depends on the size, shape and anisotropy of the colloidal particles. So, the colloid-optic method is potentially of great value in enabling one to ascertain the particle size, shape and anisotropy.

The degree of depolarisation is expressed as the ratio of the weaker component to the stronger component§ in the scattered beam and is referred to as the "Depolarisation factor". Mie's theory[1] indicates that the degree of depolarisation using unpolarised incident light, *i.e.*, ρ_u becomes equal to zero if the particles are spherical, isotropic and small ($d << \lambda$). ρ_u attains a finite value as the size of the particles increases. Further Gans[2] has shown that ρ_u also increases with anisometry and intrinsic anisotropy.

An important advance in this field of colloid-optics has been made in the laboratories of Sir C. V. Raman in employing incident polarised light.[3] By this technique it is possible to determine ρ_v and ρ_h separately which, being simpler quantities, may be expected to be more easily correlated with the characteristics of the scattering particles. A finite value of ρ_v indicates shape, anisometry and structural anisotropy. The deviation of ρ_h from unity

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§ To avoid ambiguity it would be better to define P_h as the ratio of the vertical to the horizontal component. It is no doubt true that Krishnan effect (*Proc. Indian Acad. Sci.*, 1941, 14, 230) holds normally. It has been found by us that when the multiple scattering is large and the observation is by the "Limited Background" method, the Krihnan effect is not obeyed [Table I, 1st value]. Moreover, it is well known that Krishnan effect may not hold for systems in which particles are subjected to an orientating field.

indicates finite size. This deviation also indicates deviations from sphericity and isotropy. Krishnan[4] has derived from theoretical considerations, the relation:

$$\rho_u = \frac{1+\frac{1}{\rho_h}}{1+\frac{1}{\rho_v}} \qquad (1)$$

This is known as the reciprocity theorem and is sometimes referred to as the Krishnan effect. The equation holds for systems in which the particles are distributed at random, and has been confirmed experimentally by a large number of workers in the field, of whom mention may be made of Krishnan,[4] Boutaric and Breton[5] Hoover, Putnam and Wittenberg.[6]

An attempt is made in the present work to study the depolarisation of light scattered by a few sols of known shape and size.

2. Experimental

Preparation of Sols.—The silver iodide and stearic acid sols used in this work were prepared by the methods described previously.[7] The size of the particles in the sols was determined by the ultramicroscope.[7]

An examination of the sol with regard to (*a*) Schlierung, (*b*) twinkling under the ultramicroscope, (*c*) electric double refraction, (*d*) stream double refraction and (*e*) changes in Tyndall intensity brought about by the electric field and the flow, showed that the silver iodide sol consists of particles which are practically isometric whereas the stearic acid sol contains anisometric particles. The adoption of the Langmuir pipette technique[8] has revealed that the stearic acid particles are disc-shaped.[7]

Optical Apparatus.—The arrangement of the apparatus is diagrammatically shown in Fig. 1.

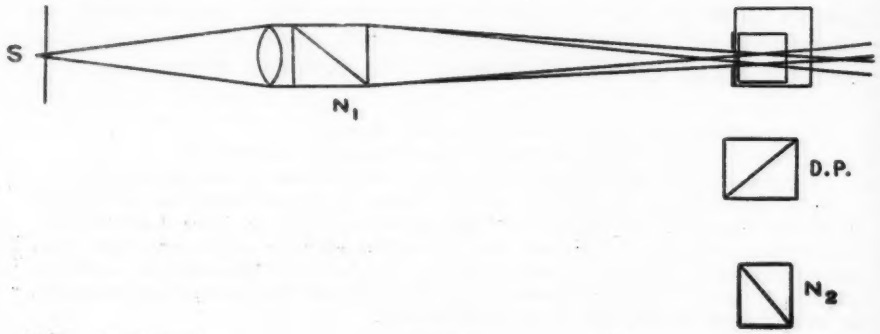

Fig. 1

S, the source of light, is a 500 C.P. point-o-lite lamp housed in a chamber having an aperture for the beam to pass. The beam was condensed by means of a lens and defined by an Ehrlich stop placed before the cell. The cell itself is placed inside a bigger cell filled with water. The outer cell is darkened by means of black paper. The polarisation of the incident light could be adjusted by rotating the nicol Nl. The scattered light was studied by employing the two methods (*a*) having the natural background (*i.e.*, viewing the entire beam of the incident light transversely) and (*b*) having a limited background (*i.e.*, viewing the scattered light through an Erlich stop 2 m.m. square). This was done with a view to see if any correlation exists between the two methods of study. The depolarisation was determined employing the Cornu method. The scattering was observed exactly at 90° to the incident beam. It was found that the two images as seen in the Cornu apparatus were of slightly different colours so that matching was difficult. The precision in matching was greatly improved by using a red filter. Eight readings at least were taken of the angle corresponding to each of the depolarisation values and the mean used in the calculations. The average error in the matching did not exceed $\pm 0{\cdot}2°$.

3. Results

The depolarisation factors for silver iodide sol B got by using the natural background, and limited background are given in Table I. The dilution of the sol in the experiments, was always done maintaining the concentration of the peptising ion constant.

Table I

Effect of nature of the background on the depolarisation values and the dilution effect

Sol used : Silver iodide sol B.

C = Concentration of the undiluted sol : 0·25 g of silver iodide per 100 c.c. of solution.

Average size of the particles = 104·8 m.μ

Number of particles per c.c. in undiluted sol = $7{\cdot}32 \times 10^{11}$.

Concentration of the sol	Natural background			Limited background
	ρ_μ	ρ_v	ρ_λ (cal.)	ρ_μ
C ..	0·133	0·065	0·85	0·305
C/2 ..	0·085	0·034	0·64	0·175
C/4 ..	0·066	0·021	0·44	0·137
C/8 ..	0·052	0·016	0·46	0·123
C/16 ..	0·052	0·016	0·46	0·125
C/32 ..	0·052	0·017	0·49	..

With a view to finding out whether the reciprocity theorem holds for limited background, the values of ρ_μ, ρ_v and ρ_k were determined for sol A employing the limited background, for various dilutions. The results are given in Table II. In order to investigate the effect of size on the depolarisation values at different dilutions, the particles of the silver iodide sol B were

TABLE II

Krishnan effect and limited background

Sol used : Silver iodide sol A

$\theta_k = \log \sin^{-1} \left\{ \begin{matrix} \text{Conc. } 0{\cdot}5\% \\ \log \sin \theta_v - \log \tan \theta_k \end{matrix} \right\}$

Concentration of the sol.	θ_μ	θ_v	θ_k (obs).	θ_k (calc.)
C ..	36·4°	33·0°	45·8°	47·6°
C/2 ..	32·0°	25·5°	43·2°	43·5°
C/4 ..	27·0°	19·05°	40·1°	39·8°
C/8 ..	24·25°	16·1°	38·1°	37·9°
C/16 ..	21·6°	13·7°	36·6°	36·7°
C/32 ..	19·15°	11·6°	..	35·4°
C/64 ..	19·45°	11·6°	..	34·7°
C/128 ..	19·3°	11·6°	..	35·2°

made to grow by the addition of 10 c.c. of 0·1 N potassium iodide to 10 c.c. of the sol. Measurements of ρ_μ of the resulting sol BB were made at different dilutions. The size of the particles in sol BB was determined by using the ultramicroscope as described previously.[7] The results are given in Table III.

TABLE III

Effect of aggregation on depolarisation: Natural background

C = 0·25 g of silver iodide per 100 c.c. of the sol.

Number of particles per c.c. in sol of concentration C/2 in sol B = $3{\cdot}66 \times 10^{11}$.

Number of particles per c.c. in sol of concentration C/2 in sol B B = $2{\cdot}6 \times 10^{10}$.

Concentraiion	ρ_μ of original sol. 'B' (size 104·8 m.μ	ρ_μ of aggregated sol. BB (size 254 m.μ
C/2 .	0·085	0·124
C/4 ..	0·066	0·099
C/8 ..	0·052	0·089
C/16 ..	0·052	0·079
C/32 ..	0·052	8·080
C/64 ..	0·052	0·081

The effect of temperature on depolarisation was next investigated. The results obtained with silver iodide (sol B), are given in Table IV. Effect of the width of the slit on the values of depolarisation is given in Table V. The effect of dilution on the depolarisation of stearic acid sol is given in Table VI.

TABLE IV

Effect of temperature on depolarisation

Sol used : silver iodide sol B.
Natural background.

ρ_u at 23° C.	ρ_u at 60° C.
0·068	0·070

TABLE V

Effect of width of slit on depolarisation

Sol used : Silver iodide sol B.
Natural background.

Concentration	ρ_u with a slit of 2 mm. square	ρ_u with a slit of 1 mm. square
C ..	0·133	0·092
C/32 ..	0·052	0·052

TABLE VI

Depolarisation of stearic acid sol

Natural background.
C = concentration of the original sol = 0·085%.
Size = 390·8.

Concentration	ρ_u	ρ_v	ρ_h (obs.)	ρ_h (Calc.)
C	0·087	0·050	0·57	0·52
C/2	0·066	0·026	*	0·68
C/4	0·048	0·022	*	0·82
C/8	0·034	*	*	..
C/16	0·034	*	*	..

* These values could not be taken on account of the low intensity of scattering of Tyndal light.

4. DISCUSSION

1. *Effect of nature of the background on depolarisation.*—An examination of Table I shows that the values of depolarisation differ according as the background is natural or limited. With the natural background, the effect of the depolarisation of the light from the background gets cancelled out and so the true values of depolarisation are obtained. With the limited background, only apparent and not true values

are got. It was also found that the depolarisation value as determined by the limited background method was found to be affected by distance travelled by the incident and the scattered beams through the colloid during observation. No such effect was noticed by the natural background technique. It is however of interest to note that the change of depolarisation with dilution is similar in the two modes of observation. An examination of Table I shows that the depolarisation decreases with dilution in both the cases. Moreover the final constant value is reached in either case, at a concentration of C/8.

It is of interest to examine as to whether the reciprocity theorem is applicable to the data on the apparent depolarisation values got by the limited background method. A slight deviation from the normal procedure has been adopted in the present work in examining the reciprocity theorem. On the basis of the reciprocity theorem it can be easily shown that

$$\log \sin \theta_h = \log \sin \theta_v - \log \tan \theta_u \qquad (2)$$

where

θ_v, θ_h and θ_u are related to ρ_v, ρ_h and ρ_u

by the equation $\tan^2 \theta = \rho$. The value of θ_h calculated by the equation (2) is compared with the value of θ_h actually observed in the Cornu apparatus. These values are given in Table II. An examination of the Table shows that the reciprocity theorem holds very well indeed even for the observation with the limited background. At the highest concentration however, there is a deviation both from the Krishnan effect (in that $\theta_h > 45°$) and the reciprocity theorem. This deviation is not due to any increased influence of the experimental error in this region. For, it can be shown by an application of the theory of errors that, the error $\delta\theta_h$ in the calculation of θ_h from the errors in the values of θ_u and θ_v is given by the equation

$$\frac{\rho_h \rho_u \sin 2\theta_h}{\rho_u} \left\{ \frac{\delta\theta_v}{\sin 2\theta_v} - \rho_v \cdot \frac{\delta\theta_u}{\sin 2\theta_u} \cdot \frac{1}{\sin^2 \theta_v} \right\}$$

An application of this equation to the present case, shows that the error introduced in the final result is of the same order throughout the range of the experimental data used in the calculation. This deviation from the reciprocity theorem is real as also is the deviation from the Krishnan effect. Both of these effects are probably due to high multiple scattering that occurs in the highly concentrated colloidal solution, which introduces a high and complex background effect in the limited background method of observation.

2. *Effect of concentration on depolarisation.*—An examination of Tables I, II, III and VI shows that, on diluting the sols, the depolarisation

at first exhibits a change and then remains constant with both the Sols investigated in the present paper. This is in agreement with the observation of G. Sharada Bai, Doss and Rao,[9] on clay sols and by Hoover and others[6] on bentonite sols.

The change is exhibited by all the three depolarisation factors alike as can be seen from the Table I. The values reach the constant value at a concentration of C/8 in all the three cases. ρ_h (Table II) no doubt, attains the final value a little earlier but this is due to the fact that the variation in the values of ρ_h with concentration is comparatively small. In general, the depolarisation factors decrease with dilution. But with stearic acid sol, ρ_h definitely increases with dilution. This exceptional behaviour which is probably connected with disc-shaped possessed by the particles, needs elucidation.

The change of depolarisation is not due to any change in particle size since it is not likely to occur in our system wherein the ion environment has been maintained constant during dilution. The change of depolarisation with change in concentration is therefore to be ascribed to the other factors: (*a*) Molecular field effect of Gans[11] and (*b*) multiple scattering.[10] We shall first discuss the former. The field effect may be considered to a first approximation, as due to a close mutual approach of the particles so that the group would have different scattering properties as compared with what it would be if the particles acted independently. The probability of occurrence of such proximity can be computed by adopting statistical methods. Let us assume that the molecular field effect becomes appreciable only when two or more particles are contained within a sphere of diameter d. The volume of such a sphere is $0{\cdot}52\,d^3$. The probabilities P_1 and P_2 of finding singles and pairs respectively in that volume is given by (12):

$$P_1 : P_2 :: 1 : \nu/2$$

where ν is the average number of particles contained in that sphere.

Let us apply this idea to silver iodide sol B. A noticeable effect of concentration on depolarisation begins at a concentration of C/4 which corresponds to $1{\cdot}8 \times 10^{11}$ particles per c.c.

$$\therefore \quad \nu = 1{\cdot}8 \times 10^{11} \times 0{\cdot}52\,d^3$$
$$= 9{\cdot}36 \times 10^{10}\,d^3.$$

If we assume that the particles are to be within a distance of about 4000 A°, in order to get the required interaction, we should have,

$$\text{for Ag I sol B,} \quad \nu/2 = \frac{9{\cdot}4 \times 10^{11}}{2} \times (4 \times 10^{-5})$$
$$= 3 \times 10^{-8}.$$

Similarly, the $\nu/2$ for Ag I sol BB, and steriac acid sol work out to be $1{\cdot}1 \times 10^{-4}$ and $1{\cdot}3 \times 10^{-4}$ respectively. From these calculations we come to the conclusion, that the effect of this interaction may vary enormously in the different cases. Whereas with silver iodide sol B, the pairs should occur to the extent of 0·3% to bring about a certain amount of interaction, it is sufficient to have only 0·01% of the pairs to produce a similar effect in silver iodide sol BB and stearic sol. Moreover, the idea that 0·01% of the pairs would upset the value of depolarisation is itself not plausible. We have no doubt neglected the occurrence of higher order clusters; but their probability of occurrence is much smaller and need not be taken into account. We have no doubt assumed a value of 4000 A° for *d*. Assumption of any other plausible value does not remove the difficulty.

The above considerations lead us to the conclusion that the effect due to molecular field is small and any observed large changes in depolarisation should be due to the other factor multiple scattering. The fact that the concentration effect becomes more considerable as the particle size increases also points to the same conclusion. Larger the particle size, larger the scattering and larger would be the influence of multiple scattering. In fact, the ferric oxide sol which contains very fine particles scatters light to a very small extent, shows no change of depolarisation with increase in concentration.[6] The existence of multiple scattering was confirmed by the fact that the depolarisation value depended upon the width of the incident beam, in the more concentrated solutions as can be seen from Table V. We agree with Hoover and co-workers[6] in emphasising on the importance of finding out the value of depolarisation at infinite dilution for use in any theoretical considerations.

The value of the concentration at which the constancy of ρ occurs is very sensitive to changes in particle size. It appears possible to take advantage of it in the determination of average size of the particles. Since ρ_u shows the effect as well as the other fectors, and the effect can also be observed with the limited background, the size can easily be determined by measuring ρ_u using the limited background method. It is necessary, of course, to find out the emperical relation between the particle size and the concentration at which a definite percentage deviation of ρ_u occurs (from the limiting value).

3. *Effect of temperature on depolarisation.*—Table IV shows that in the case of Ag I sol, temperature has very little effect on the depolarisation of light.

The function $\frac{10\rho_u}{6-7\rho_u}$ is suggested to be a measure of the anisotropy of the scattering centres. That this cannot be true with systems such as

those worked by us, becomes obvious by the fact that the value of the function for stearic acid sol is smaller than that for silver iodide sol, though the former contains particles which are highly anisotropic and the latter have no sensible anisotropy as conclusively shown by other data. A similar anomaly occurs even if the corresponding ρ_v function is considered. This made us suspect that the observed phenomenon may be connected with the small difference in refractive index between the disperse and the continuous phases. In order to test out this idea, the refractive index of the medium was changed by the addition of glycerine maintaining ionic strength constant. Even when the refractive index was made almost equal to that of stearic acid, as could be seen by the enormous fall in the intensity of scattering, the ρ_u was not detectably affected. Again the value of ρ_h for the stearic acid sol is larger than the same for the silver iodide sol, though the latter has smaller and anisotropic particles. These observations have to be taken into account in any theory proposed for explaining the depolarisation of light scattered by colloids.

ACKNOWLEDGMENT

The authors wish to place on record their grateful thanks to Sir C. V. Raman for having kindly lent the necessary apparatus for the depolarisation measurements and for his kind and instructive discussions.

6. SUMMARY

1. Measurements of ρ_u, ρ_v and ρ_h have been carried out with stearic acid sol (anisometric particles) and silver iodide sol (isometric particles), containing particles of known size.

2. That the limited background technique yields only apparent depolarisation values, has been confirmed.

3. The reciprocity theorem is found to hold exactly even with the limited background observations, except at the highest concentrations (0·5%).

4. It is shown that molecular field effect of Gans cannot account for the variation of depolarisation with concentration. Multiple scattering adequately accounts for the phenomenon.

5. The possible application of depolarisation studies at the different concentrations for the determination of particle size is indicated.

6. Temperature is found to have no sensible effect on depolarisation of silver iodide sol.

7. Difficulties in correlating ρ_u, ρ_v and ρ_h with size and anisotropy have been pointed out.

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PHOTOELASTIC CONSTANTS OF DIAMOND CORRECTIONS

By G. N. Ramachandran

(Communicated by Sir C. V. Raman)

In a paper having this title (*Proc. Ind. Acad. Sci.*, **25**, 1947, 208) Table IV, on p. 217, contains a numerical error as a result of which the piezo-optic constants of diamond appear to be about 100 times smaller than for other cubic crystals studied by Pockels. The error arose from the fact that Pockels' unit of pressure was gm. wt./mm.^{2}, which was wrongly taken to be gm. wt./cm.^{2}, the author's unit. The elasto-optic constants are however correct. In the table below, correct piezo-optic constants are given, but in fundamental units, *viz.*, dynes cm.$^{-2}$ for pressure and cm.^{2} dyne^{-1} for the constants. For diamond, they are of the same order of magnitude as for other crystals. It may be mentioned that potassium and ammonium alums belonging to the T_h class of the cubic system have four piezo-optic constants the values of which in 10^{-13} cm.^{2} dyne^{-1} are (Bhagavantam and Suryanarayana, *Proc. Ind. Acad. Sci.*, 1947, **26**, 97):

$$q_{11} - q_{12} = -5{\cdot}45,\ q_{11} - q_{13} = -4{\cdot}84,\ q_{44} = -0{\cdot}65,\ q_{11} = 3{\cdot}0$$

Table of Piezo-Optic Constants

Substance	$(q_{11}-q_{12})\cdot10^{13}$	$q_{44}\cdot10^{13}$	χ	$q_{12}\cdot10^{13}$
Rocksalt ..	−1·161	−0·817	0·704	1·40
Sylvine ..	1·65	−4·14	−2·525	..
Fluorspar ..	−1·393	0·672	−0·482	1·113
Pottassium alum ..	−4·22	−0·446	0·106	..
Ammonium alum ..	−4·377	−0·759	0·173	..
Diamond ..	0·80	0·27	0·33	−0·37

(*Crystallographic Laboratory, Cavendish Laboratory, Cambridge*)

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